LUBRICANT FOR IMPROVED SURFACE QUALITY OF CAST ALUMINUM AND METHOD

Field of the Invention

[0001] The invention relates to coolant and lubricant formulations for use in the casting of aluminum or aluminum alloy ingots or bodies. In particular, lubricants and coolants containing a fluorinated species are used to improve surface quality of cast ingots or bodies, resulting in enhanced product recovery. A method for producing aluminum or aluminum alloy ingots with enhanced surface quality is also disclosed.

Background of the Invention

[0002] The casting of alloys may be done by any number of methods known to those skilled in the art, such as direct chill casting (DC), electromagnetic casting (EMC), horizontal direct chill casting (HDC), hot top casting, continuous casting, semi-continuous casting, die casting, roll casting and sand casting.

[0003] Each of these casting methods mentioned above has a set of its own inherent problems, but with each technique, surface imperfections can be an issue. It is well known in the aluminum alloy casting art that molten metal (or *melt* for brevity) surface oxidation can result in various surface imperfections in cast ingots such as pits, vertical folds, oxide patches and the like, which can develop into cracks during casting or in later processing. A crack in an ingot or slab propagates during subsequent rolling, for example, leading to expensive remedial rework or scrapping of the cracked material. One mechanical means of removing surface imperfections from an aluminum alloy ingot is scalping. Scalping involves the machining off a surface layer along the sides of an ingot

after it has solidified.

[0004] Certain alloys, such as 7050 and other 7xxx alloys as well as 5182 and 5083 are especially prone to surface defects and cracking. In the past, beryllium has been added, usually at part per million (ppm) levels to some of these alloys to control melt surface defects, and to prevent magnesium loss due to oxidation. However, beryllium has been banned from aluminum products used for food and beverage packaging. Further, there have been increased concerns over the health risks associated with factory workers using beryllium and products containing beryllium. For these reasons, suitable replacement strategies to inhibit oxidation during casting are needed.

[0005] In casting of aluminum alloys it is also well known in the art to use a mold lubricant, coolant or parting agent. The terms lubricant, coolant, and parting agent may have slightly different meanings to those skilled in the art of casting aluminum alloys, but for the purposes of the instant invention, the three terms are used interchangeably. Satisfactory ingot surface can only be obtained using a lubricant that has is effective in keeping aluminum from sticking to the mold at high temperatures used in casting aluminum alloys. In early casting practices greases were commonly employed as mold lubricants. With the advent of modern casting methods, including continuous casting, continuous lubrication with free flowing oils has replaced the use of greases as mold lubricants.

[0006] Continuous casting refers to the uninterrupted formation of a cast body or ingot. For example, the body or ingot may be cast on or between belts, as in belt casting;

between blocks, as in block casting; or in a mold or die that is open at both ends, as in direct chill (DC) casting. Casting may continue indefinitely if the cast body is subsequently cut into desired lengths. Alternately, the pouring operation may be started and stopped when an ingot of desired length is obtained. The latter situation is referred to as semi-continuous casting.

[0007] Continuous lubrication is required for fully continuous casting and offers a number of advantages for semi-continuous casting. These advantages include elimination of flame and smoke, elimination of dragging and tearing tendencies near the end of the cast and allowing casting practices that produce better quality and more uniform surfaces.

[0008] Despite the use of continuous lubrication during casting, a limitation of current ingot casting practice exists in the inadequate control of oxide growth at the meniscus of molten metal at the mold interface. Uncontrolled oxide growth at the meniscus of the molten metal and mold interface is particularly problematic of alloying elements that rapidly oxidize in air or in air containing moisture. Lithium and magnesium are examples of alloying elements that oxidize rapidly. In both cases, the vapor pressure is higher than that of aluminum and they diffuse to the surface and react with oxygen or moisture in the ambient air.

[0009] The use of atmospheres consisting of inert gases to protect the melt and ingot have been previously employed to limit ingot surface oxidation. Examples of the use of protective gases during casting are taught in U.S. Patent No. 3,087,213, U.S. Patent No. 4,770,697 and U.S. Patent No. 6,269,862.

[0010] U.S. Patent No. 4,092,159 relates to a fluoride-containing glass flux for metal casting. U.S. Patent No. 4,766,948 discloses a process for coating aluminum alloys that uses a halogen-containing salt mixture on the inner wall of a mold. U. S. Patent No. 5,415,220 relates to direct chill casting of an aluminum-lithium alloy using a protective molten salt cover having lithium chloride and at least one other salt from a group that includes lithium fluoride.

[0011] There remains a need for an effective alternative to beryllium to prevent surface imperfections, such as vertical folds, pits, oxide patches and the like from forming during aluminum ingot casting, and to prevent melt surface oxidation, particularly when casting aluminum that is alloyed with magnesium an/or lithium. Such a method would be instrumental in preventing cracks, which can form during casting or can develop in later processing. Finally, the method preferably would have no adverse affect on alloy properties.

[0012] The primary object of the present invention is to provide a lubricant composition that inhibits oxidation of metal during casting.

[0013] Another object of the present invention is to provide an economical and efficient method for minimizing or eliminating oxidation of aluminum and high vapor pressure alloying elements, such as but not limited to, magnesium and lithium at the melt / mold meniscus during continuous casting of aluminum alloys.

[0014] Yet another object of this invention is to provide a casting lubricant formulation that inhibits oxidation by producing active fluoride ions that passivate solidifying metal at casting temperatures in furnaces.

[0015] A still further object of this invention is to provide a casting lubricant that inhibits oxidation of the cast metal without requiring the use toxic and corrosive gaseous atmospheres, and thus eliminating associated emissions and equipment corrosion.

[0016] Still another object of this invention is to provide a method to inhibit oxide formation on aluminum alloy ingots or castings that does not require beryllium additions to the alloy.

[0017] These and other objects and advantages are met or exceeded by the instant invention, and will become more fully understood and appreciated with reference to the following description.

Summary of the Invention

[0018] In the present invention it has been discovered that when fluorine-containing compounds are added to conventional casting lubricants, the improved lubricant formulation can protect the surface of aluminum alloys from oxidation, and in particular from runaway magnesium or lithium alloying element oxidation, even in high humidity atmospheres.

[0019] No toxic or corrosive gases are required to practice the instant invention. Additionally, an inert atmosphere to minimize oxidation, and associated expensive furnaces and infrastructure that are required for maintaining the inert atmosphere are not

required for the practice of the instant invention.

[0020] When used in continuous casting operations, effective fluorine-containing compounds added to the casting lubricant are able to prevent oxidation from occurring at the meniscus, or where the melt contacts the mold wall. Existing continuous casting equipment for aluminum alloys can be used for this invention.

[0021] Fluorine-containing compounds are added to existing lubricant bases to prepare the oxidation inhibiting lubricant formulations of this invention. For the purposes of this invention, the fluorine-containing compounds which are effective at protecting the aluminum alloy from oxidation are referred to as fluorine-containing passivating compounds. The fluorine-containing passivating compound can be an inorganic compound, such as but not limited to, ammonium hexafluozirconate, fluorinated carbon, sodium bifluoride, potassium bifluoride, magnesium fluoride, aluminum fluoride, sodium fluoride, calcium fluoride, sodium hexafluosilicate, sodium hexafluorophosphate, potassium zirconium fluoride, sodium fluoborate, and cryolite.

[0022] Alternately, the fluorine-containing passivating compound can be an organic compound or polymer, such as but not limited to tetradecafluorohexane, polyhexafluoropropylene oxide, fluorinated ethylene propylene copolymer, perfluoroalkoxy polymers, poly(ethylene-co-tetrafluoroethylene), and polytetrafluoroethylene (Teflon® - PTFE). For organic compounds, completely fluorinated, or perfluorinated, compounds are preferred, but it is realized that partially fluorinated organic compounds, such as for example, chlorofluorocarbons or

hydrofluorocarbons fall within the scope of this invention.

[0023] Existing lubricant bases that may be used in this invention include solid lubricants, such as for example molybdenum disulfide and graphite; liquid lubricants, such as for example mineral oils; and semi-liquid lubricants, including for example waxes, greases, emulsions, dispersions, and single phase coolants. Families of existing lubricants and/or additives that can be used for this invention include, but are not limited to: mineral oils, synthetic lubricants, poly (alpha olefins), polyisobutylene, monobasic and dibasic esters, polyglycols, chlorofluorocarbons, fluorocarbons, phosphate esters, overbased sulphonates of metals, phosphonic acids and salts thereof, silicate esters, slianes, siloxanes, polyphenyl ethers, fluoroesters, neopentyl polyol esters, Teflon®, natural oils and fats (for example: castor oil, peanut oil, corn oil, canola oil, cotton seed oil, olive oil, rapseed oil, safflower oil, sesame oil, sunflower oil, soybean oil, linseed oil, coconut oil, palm kernel oil, neatsfoot oil), fatty acids, fatty alcohols, organic metal complexes, ion pairs with amine compounds, soaps, hydrogenated and semi-hydrogenated oils and fats, organic and inorganic borates, and lamellar solids.

[0024] The oxidation inhibiting lubricant formulations are mixed in a high speed mixing operation, such as blending or shearing, or any other mixing operation known by those skilled in the art to provide dispersions, emulsions, and/or true solutions. At this stage, the formulation is ready to use as a oxidation inhibiting casting lubricant.

[0025] In a preferred embodiment of this invention, glycerol trioleate is used as the conventional casting lubricant base. About 1 % by weight of fluorinated carbon, also

known in the art as fluorinated graphite, is added to the glycerol trioleate base. The mixture is then sheared in a high speed blender for about 5 minutes. The oxidation inhibiting lubricant so formulated is applied to a casting mold in any manner that is familiar to those skilled in the art of casting aluminum alloys.

[0026] In another preferred embodiment of this invention, polyalphaolefin is used as the conventional casting lubricant base. About 1 % by weight of sodium hexafluosilicate is added to the polyalphaolefin base. A preferred polyalphaolefin base is ExxonMobil SHF-101 from the ExxonMobil Chemical Company, Houston, Texas. The mixture is then sheared in a high speed blender for about 5 minutes. The oxidation inhibiting lubricant so formulated is applied to a casting mold in any manner that is familiar to those skilled in the art of casting aluminum alloys.

[0027] In a different preferred embodiment of this invention, glycerol trioleate is used as the conventional casting lubricant base. About 2 % by weight of tetradecafluorohexane, also known in the art as perfluorinated hexane, is added to the glycerol trioleate base. The mixture is then sheared in a high speed blender for about 5 minutes. The oxidation inhibiting lubricant so formulated is applied to a casting mold in any manner that is familiar to those skilled in the art of casting aluminum alloys.

[0028] In yet another preferred embodiment of this invention, glycerol trioleate is used as the conventional casting lubricant base. About 1 % by weight of sodium hexafluorophosphate is added to the glycerol trioleate base. The mixture is then sheared in a high speed blender for about 5 minutes. The oxidation inhibiting lubricant so

formulated is applied to a casting mold in any manner that is familiar to those skilled in the art of casting aluminum alloys.

[0029] In still another preferred embodiment of this invention, glycerol trioleate is used as the conventional casting lubricant base. About 1 % by weight of potassium zirconium fluoride is added to the glycerol trioleate base. The mixture is then sheared in a high speed blender for about 5 minutes. The oxidation inhibiting lubricant so formulated is applied to a casting mold in any manner that is familiar to those skilled in the art of casting aluminum alloys.

[0030] In one more preferred embodiment of this invention, an oxidation inhibiting lubricant formulation of this invention is supplied to the oil ring of a cooled continuous or semi-continuous casting mold, which subsequently lubricates the inner wall of the continuous casting mold. Molten aluminum alloy is cast into the mold. The oxidation inhibiting lubricant reduces the oxidation of the molten aluminum base alloy at the meniscus of the lubricated inner mold wall and the molten aluminum base alloy.

Brief Description of the Drawings

[0031] Figure 1 is a flowchart for preparation of the formulation of the oxidation inhibiting lubricant of the instant invention.

[0032] Figure 2 is a schematic characterization of a DC continuous casting mold used in the method of this invention.

[0033] Figure 3 is a plot of oxide thickness obtained on the surface of aluminum alloy 5182 when oxidation inhibiting lubricant formulations were placed on the alloy surface and heated to 500°C for 12 hours in air.

Detailed Description of Preferred Embodiments

[0034] The instant invention provides casting lubricant formulations and methods for using these formulations that substantially inhibit the formation of surface oxides during casting of aluminum alloys. In particular, practice of the instant invention protects the meniscus of molten aluminum alloy at the mold interface from uncontrolled oxidation.

[0035] Practice of this invention protects the surface of molten and solid aluminum alloys from oxidation even in high humidity. Furthermore, the instant invention is effective in protecting aluminum alloy surfaces from oxidation, even for aluminum alloys containing lithium and magnesium.

[0036] Referring now to Figure 1, a flowchart for preparation of the oxidation inhibiting lubricant of this investigation is presented. The invention improves on existing lubricants used in the casting of aluminum and aluminum base alloy ingots and forms, and in the general manufacture of aluminum products, using thermomechanical processes such as, but not limited to, casting, extrusion, hot and cold rolling, and forging.

[0037] In a preferred embodiment, an existing aluminum alloy casting lubricant, glycerol trioleate, is used as the lubricant base. About 1 % by weight of fluorinated carbon, also known in the art as fluorinated graphite, is added to the glycerol trioleate

base. The mixture is then sheared in a high speed blender for about 5 minutes. The oxidation inhibiting lubricant so formulated is applied to a casting mold in any manner that is familiar to those skilled in the art of casting aluminum alloys.

[0038] In another preferred embodiment of this invention, glycerol trioleate is used as the conventional casting lubricant base. About 2 % by weight of tetradecafluorohexane, also known in the art as perfluorinated hexane, is added to the glycerol trioleate base. The mixture is then sheared in a high speed blender for about 5 minutes. The oxidation inhibiting lubricant so formulated is applied to a casting mold in any manner that is familiar to those skilled in the art of casting aluminum alloys.

[0039] In yet another preferred embodiment of this invention, glycerol trioleate is used as the conventional casting lubricant base. About 1 % by weight of sodium hexafluorophosphate is added to the glycerol trioleate base. The mixture is then sheared in a high speed blender for about 5 minutes. The oxidation inhibiting lubricant so formulated is applied to a casting mold in any manner that is familiar to those skilled in the art of casting aluminum alloys.

[0040] In still another preferred embodiment of this invention, glycerol trioleate is used as the conventional casting lubricant base. About 1 % by weight of potassium zirconium fluoride is added to the glycerol trioleate base. The mixture is then sheared in a high speed blender for about 5 minutes. The oxidation inhibiting lubricant so formulated is applied to a casting mold in any manner that is familiar to those skilled in the art of casting aluminum alloys.

[0041] The choice of a preferred fluorine-containing passivating compound can be determined by the intended use of the oxidation inhibiting lubricant, for example, the use of the lubricant for casting aluminum alloys at a particular melt temperature. While not intending to be bound by any particular theory, it is hypothesized that at or below the operating temperature of the processing step the fluorine-containing passivating compound in the oxidation inhibiting lubricant of this invention breaks down to supply a active fluoride species to the solidifying aluminum alloy surface. The term "active fluoride" for purposes of this invention, means a fluorine species that is capable of reacting directly with the metal to form a metal fluoride, or one that can displace a metal oxide to form a metal fluoride. Since fluorine is the most electronegative element on the periodic table of the elements, active fluorides can displace the oxide on the solidified metal surface and form metal oxy-fluoride surface compounds. If sufficient fluoride is present, the entire metal oxide can be converted to a metal fluoride, thus preventing oxidation of the metal surface in air or humid air.

[0042] Based on the above hypothesis, it is surprising that certain fluorine-containing passivating compounds are effective in the oxidation inhibiting lubricant of this invention. For example, experiments have shown that 1% magnesium fluoride in glycerol trioleate is an effective oxidation inhibiting lubricant formulation for minimizing oxidation of aluminum alloy 5182. The melting point of magnesium fluoride is 1261°C (*"CRC Handbook of Chemistry and Physics, 65th Edition*, CRC Press, Inc., Boca Raton, FL, 1985), well above the liquidus of most aluminum alloys. It is speculated that the

enough magnesium fluoride decomposes in the oxidation inhibiting lubricant at the aluminum alloy casting temperature to provide the 5182 aluminum alloy surface with sufficient fluoride to prevent oxidation, even though the temperature during casting is substantially below the melting point of magnesium fluoride.

[0043] A major benefit of the oxidation inhibiting lubricant of this invention is realized in preventing oxidation of aluminum and its alloying elements at the meniscus during DC casting of aluminum. However, it is recognized by those skilled in the art that the oxidation inhibiting lubricant of this invention can be used in any thermomechanical processing of aluminum and its alloys. These processing steps include, but are not limited to casting, hot and cold rolling, forging, and extrusion. A fluorine containing passivating compound can be selected to be effective at the operating temperature of the thermomechanical process being considered for use with the oxidation inhibiting lubricant of this invention.

[0044] Fluorine containing passivating compounds that are effective for the practice of this invention include, but are not limited to, ammonium hexafluozirconate, fluorinated carbon, sodium bifluoride, potassium bifluoride, magnesium fluoride, aluminum fluoride, sodium fluoride, calcium fluoride, sodium hexafluosilicate, sodium hexafluorophosphate, potassium zirconium fluoride, tetradecafluorohexane, cryolite, polyhexafluoropropylene oxide, fluorinated ethylene propylene copolymer, perfluoroalkoxy polymers, poly(ethylene-co-tetrafluoroethylene), and polytetrafluoroethylene.

[0045] Referring now to Figure 2, a cross-section of a DC casting mold **10**, which can be used to cast aluminum alloy ingots according to the instant invention, is schematically depicted. The DC casting mold **10** comprises molten metal **11** from a furnace. The molten metal is held in a trough **12**. A control pin **13** activates and deactivates the flow of molten metal **11** into a distributor bag **14**, which distributes the molten metal into the cooled mold **15**. The molten metal **11** in the cooled mold **15** may form an oxide skim **16**. The inner wall **17** of the cooled mold **15** is cooled by a water cooling jacket **18** that cools the mold **15** and floods the solidified ingot surface **19** with cooling water **20**. The inner wall **17** is also lubricated with an oxidation inhibiting formulation of the instant invention by using an oil ring **21** positioned at or near the meniscus of where the molten metal **11** in the mold **15** contacts the inner wall **17** of the cooled mold **15**. In a preferred embodiment, the oxidation inhibiting lubricant comprises 1% fluorinated carbon in a glycerol trioleate base. In another preferred embodiment, the oxidation inhibiting lubricant comprises 1% fluorinated carbon in a polyalphaolefin base. Molten metal **11** in the mold **15** solidifies into a solidified ingot **22**. The solidified ingot **22** rests on a starting block **23**. The starting block **23** rests on a starting block holder **24**. The starting block holder **24** is attached to a platen **25**. The platen can be lowered or raised by a cylinder ram **26**. As molten metal **11** in the mold **15** solidifies into solidified ingot **22**, the cylinder ram **26** is lowered, which causes the solidified ingot **22** to also be lowered according to the directional arrows **27** superimposed onto the schematic cross section of the DC mold **10**. As the cylinder ram **26** and solidified ingot **22** are lowered

the control pin **13** is activated to allow more molten metal **11** in the trough **12** to flow into the cooled mold **15** via the distributor bag **14**, and ingots of aluminum alloy are cast, the length of such ingots being constrained only by the movement of the cylinder ram **26**. During the ingot casting operation, the solidified ingot **22** in contact with the inner wall **17** is continuously lubricated with the oxidation inhibiting lubricant of this invention via the oil ring **21**, thusly providing a process for minimizing oxidation of the ingot and undesirable surface defects that were described earlier. During practice of this invention, there is no requirement for the undesirable practice of alloying the aluminum with beryllium, nor is there any reliance on using toxic gases such as ammonium fluoborate or boron trifluoride to prevent oxidation during casting.

[0046] To test the efficacy of the oxidation inhibiting lubricant formulations, several oxidation inhibiting lubricants were formulated according to the teachings of this invention as described in the following examples. The oxidation inhibiting lubricants so formulated were placed onto the surface of a sheet aluminum alloy 5182, which was then heated in a furnace at 500°C for 12 hours. The areas of the 5182 sheet that were covered with the oxidation inhibiting lubricants were analyzed for oxide thickness as measured by Auger electron spectroscopy (AES) depth profiling. The results of the AES oxide thickness measurements are presented graphically in Figure 3 and in the Examples found below.

<u>EXAMPLE 1</u>

[0047] About 1% by weight of ammonium fluozirconate was added to a glycerol

trioleate base. The mixture was sheared in a high speed blender for about 5 minutes. After placing the lubricant on the 5182 sheet and heating as described above, the oxide thickness was measured as 975 Angstroms (Å).

EXAMPLE 2

[0048] About 1% by weight of fluorinated graphite was added to a glycerol trioleate base. The mixture was sheared in a high speed blender for about 5 minutes. After placing the lubricant on the 5182 sheet and heating as described above, the oxide thickness was measured as 1,050 Angstroms (Å).

EXAMPLE 3

[0049] About 1% by weight of zirconium tetrafluoride was added to a glycerol trioleate base. The mixture was sheared in a high speed blender for about 5 minutes. After placing the lubricant on the 5182 sheet and heating as described above, the oxide thickness was measured as 1,300 Angstroms (Å).

EXAMPLE 4

[0050] About 0.5% by weight of polytetrafluoroethylene (PTFE) was added to a glycerol trioleate base. The mixture was sheared in a high speed blender for about 5 minutes. After placing the lubricant on the 5182 sheet and heating as described above, the oxide thickness was measured as 1,350 Angstroms (Å).

EXAMPLE 5

[0051] About 1% by weight of sodium fluoborate was added to a glycerol trioleate base. The mixture was sheared in a high speed blender for about 5 minutes. After

placing the lubricant on the 5182 sheet and heating as described above, the oxide thickness was measured as 1,300 Angstroms (Å).

EXAMPLE 6

[0052] About 1% by weight of hydrated sodium hexafluosilicate was added to a glycerol trioleate base. The mixture was sheared in a high speed blender for about 5 minutes. After placing the lubricant on the 5182 sheet and heating as described above, the oxide thickness was measured as 1,400 Angstroms (Å).

EXAMPLE 7

[0053] About 1% by weight of anhydrous sodium hexafluosilicate was added to a glycerol trioleate base. The mixture was sheared in a high speed blender for about 5 minutes. After placing the lubricant on the 5182 sheet and heating as described above, the oxide thickness was measured as 1,500 Angstroms (Å).

EXAMPLE 8

[0054] About 0.03% by weight of anhydrous sodium hexafluosilicate was added to a glycerol trioleate base. The mixture was sheared in a high speed blender for about 5 minutes. After placing the lubricant on the 5182 sheet and heating as described above, the oxide thickness was measured as greater than 10,000 Angstroms (Å). It is speculated that the concentration of the fluorine containing passivating compound in the lubricant was insufficient to prevent oxidation of the 5182 sheet as it was heated at 500°C for about 12 hours.

EXAMPLE 9

[0055] About 1% by weight of potassium iodide was added to a glycerol trioleate base. The mixture was sheared in a high speed blender for about 5 minutes. After placing the lubricant on the 5182 sheet and heating as described above, the oxide thickness was measured as greater than 10,000 Angstroms (Å). Potassium iodide is not a fluorine containing passivating compound and was not effective in the formulation of an oxidation inhibiting lubricant as taught by the instant invention.

[0056] Having described the presently preferred embodiments, it is to be understood that the invention may be otherwise embodied within the scope of the appended claims.